

REMARKS

This Preliminary Amendment cancels the original claims, without prejudice, in the underlying PCT Application No. PCT/EP2004/052269. The Preliminary Amendment also adds new claims 21-40. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.125(b), the Substitute Specification (including the Abstract) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to United States Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. §§ 1.121(b)(3)(ii) and 1.125(c), a Marked-Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) are respectfully requested.

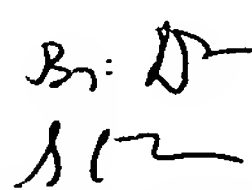
The underlying PCT Application No. PCT/EP2004/052269 includes an International Search Report, dated July 22, 2005, a copy of which is submitted herewith.

Applicants assert that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully submitted,

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ELECTROLYTIC METHOD FOR PHOSPHATING METALLIC SURFACES
AND METAL LAYER PHOSPHATED THEREBYField Of The Invention

The present invention generally relates to an electrolytic method for the phosphating of metal surfaces, ~~according to the definition of the species in Claim 1.~~ It also relates to a phosphated metal layer produced with the aid of this method.

5 Background Information

Zinc phosphating is a widespread method for the corrosion protection of low alloyed steels. In this connection, in a pH-controlled precipitation reaction, zinc phosphate crystals (hopeite) are deposited on the component part surface. In order to be able to deposit a phosphate layer, the solubility product of the zinc phosphate has to be exceeded. This occurs by an attack (pickling)
10 on the base metal (e.g. $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$). The electrons liberated in this context are used for proton reduction. The pH is shifted in the direction of neutral to basic, and the solubility product is exceeded. Normally, layers 2-3 μm in thickness form in this context, which have a degree of coverage of ca. 90 to 95%. The corrosion protection is limited by the thin and porous layer that is created, and is therefore usually combined with other coatings, such as
15 corrosion-protective oil or KTL. Further developments aim at increasing corrosion protection while doing without such additional coatings.

One attempt at achieving thicker layers is the use of electrolytic current. Because of the electrolytic reaction, the result is a pH shift that is able to be influenced, and therewith the control of the layer growth.

20 ~~JP-A~~ Japanese Published Patent Application No. 85/211080 relates to a method for producing anticorrosion layers on metal surfaces with the aid of zinc phosphating solutions under intermittent application of a cathode current. In this connection, a corrosion-resistant protective layer is produced also at the edges of the metal surfaces that are to be treated.

A similar method is described in ~~EP-A~~ European Published Patent Application No. 0 171 790.
25 In this instance, subsequently to usual zinc phosphating, the metal surfaces are treated with an

acid aqueous solution containing zinc ions, phosphate ions and chloride ions, a direct current being applied at the same time to the anodically connected metal surfaces.

A method is known from ~~DE~~*German Published Patent Application No. 41 11 186-A1* for the phosphating of metallic surfaces, especially of electrolytically zinc coated or hot dip

5 galvanized steel band surfaces by treatment using dipping or spray dipping using, acidic aqueous phosphating solutions, at the same time, the work pieces being treated cathodically using a direct current. In this context, one works with a phosphating solution containing the following components: Zn^{2+} cations in the range of 0.1 to 5 g/l; PO_4^{3-} anions in the range of 5 to 50 g/l; NO_3^- anions in the range of 0.1 to 50 g/l; and Ni^{2+} cations in the range of 0.1 to 5 g/l,
10 and/or Co^{2+} cations in the range of 0.1 to 5 g/l.

The pH value of phosphating solutions, in this context, lies in the range of 1.5 to 4.5 and the temperature of the phosphating solutions lie in the range of 10 to 80°C,

The current density of the direct current, with which the work pieces are treated cathodically
15 during phosphating, amounts to between 0.01 and 100 mA/cm².

The disadvantage with conventional phosphating methods is that they are limited to low alloy steels, as well as Zn and Al, and that they are made up of zinc phosphate crystals, and have no cathodic corrosion protection. Besides that, in most cases an added activation is required.

Summary of the ~~Of~~ The Invention

20 The method, according to the present invention, for phosphating metal surfaces has the advantage over the related art that compact layers are developed, whose thickness is able to be adjusted almost at will.

An additional advantage is that the layers generated have a clearly greater corrosion resistance.

Furthermore, it is advantageous that the phosphating is able to take place free of activation.

25 ~~Advantageous further developments of the present invention result from the measures indicated in the dependent claims.~~

Thus, for example, the electrolysis is performed either in a potentiostatic or a galvanostatic manner or a mixture of the two components.

~~Brief Description of the Drawing~~ An exemplary embodiment of the present invention is

5 ~~represented in the drawing and elucidated in greater detail in the following description. The figure~~
Of The Drawing

The Figure shows a diagrammatic sketch of the production method according to the present invention.

~~Exemplary Embodiments~~

10 Detailed Description

The aim of the present invention is the development of an electrolytic coating method for phosphating metal surfaces, in which the pores in the phosphate layer are filled in by metallic zinc or zinc alloys. In the method according to the present invention, the electrolytic zinc or zinc alloy depositing takes place simultaneously with the zinc phosphate crystal formation in
15 the same electrolyte. By contrast to the usual phosphating, in which, after cleaning and pickling, the work piece was dipped into a titanium phosphate suspension (ca. 60 s at a pH ~ 9), the method according to the present invention is able to do without an added activation process. The speed of layer formation is extraordinarily rapid, at ca. 3 to 20 $\mu\text{m}/\text{min}$ at current densities of $j = -10$ to $-50 \text{ A}/\text{dm}^2$. In conventional methods used up to now, depositing was only at ca. 1
20 $\mu\text{m}/\text{min}$. Using the method described, besides directly coating low alloy steels, one may also directly coat stainless steels as well as other noble and non-noble materials, such as Al, Al alloys, Cu, Cu alloys, Ni, Ni alloys, etc. However, in currentless methods it is only possible to deposit on materials that permit a corrosive pickling attack, since otherwise the above-described pH shift, that is required, will not occur. In this context, the electrolysis may
25 be controlled both potentiostatically and galvanostatically, or may be carried out using a mixture of the two components.

In the method according to the present invention, compact layers form, which have the distinction that the spaces between the zinc phosphate crystals are filled in by a network of metallically deposited zinc or zinc alloy. Because of the simultaneous formation of electrically
30 conductive zinc or zinc alloy, a pH shift induced by electrolysis is able to take place, that is, the electrons are supplied from the outside, and almost any layer thickness growth desired of the zinc(zinc alloy)/zinc phosphate layer may be achieved by the reduction of H^+ at the zinc surface.

The figure shows a diagrammatic sketch of the production method according to the present invention. In this context, in a usual electrolysis cell 10, having a working electrode 11 made of the corresponding base metal and a counter-electrode 12, zinc/zinc phosphate layer 14 is deposited by electrolyte 13 onto base metal 11. As indicated before, by contrast to standard phosphating, the electrodes required here for the pH shift do not originate from the iron corrosion from the low alloy steels (pickling attack on the base metal) but from an external current source 15. This protective current, among other things, also assures that base metal 11 is not attacked.

With the aid of the method according to the present invention, closed, that is, largely nonporous mixed layers (having metal, e.g. zinc, zinc/nickel, filled in phosphate layers not having exposed base metal) of approximately 3 μm to approximately 500 μm may be deposited in practically unlimited fashion. Whereas, in a salt spray test, a conventionally generated layer demonstrates a resistance of ca. 5 hours to red rust formation, by having a 20-30 μm zinc/zinc phosphate mixed layer, a resistance of more than 1000 hours could be achieved in the salt spray test. Even after a phosphating time of 30 seconds, the corrosion resistance is above 420 hours.

The coating method according to the present invention may be carried out in generally customary electrolysis cells. In this context, the counter-electrode may be made both of noble sheet metals, such as platinum, Pt/Ti or gold, and of non-noble sacrificial anodes, such as Zn, Ni, Fe, which assure a continuous subsequent transport of metal ions. As working electrodes, on which the layers are deposited (base metal), stainless steels as well as bronze, Cu, Cu alloys, Ni, Ni alloys, etc. may be used. The electrolyte will essentially be an electrolyte that is the same as is used in outside currentless phosphating. The electrolyte, in this context, contains, for instance:

Zn^{2+} : 5-50 g/l

H_2PO_4^- : 5-80 g/l

In this connection it is important that a so-called high zinc bath is used, whose zinc content is greater than 5 g/l, whereas in the normally used low zinc baths the zinc content is only about 1 – 5 g/l, in which no elementary zinc deposit or zinc alloy deposit between the phosphate crystals takes place.

In addition, the electrolyte may contain ions of elements that are able to form an alloy with zinc, so that when there is a deposit of a phosphating layer, a deposit of zinc alloys takes place simultaneously. The addition of nanoparticles and organic molecules is also conceivable. Further possible bath additives, to modify the layers, are polyphosphate, borate, organic polyhydroxy compounds, glycerophosphate and fluoride. When it comes to the additional ions,

for instance, ions may be involved of a divalent metal M, the additional divalent metal M being selected from the group consisting of Ni, Fe, Co, Cu, Mn and the like.

The reaction may be carried out with or without the addition of an accelerator. As the accelerator, the following come into consideration: urea, nitrites, chlorates, bromates,

5 hydrogen peroxide, ozone, organic nitro bodies, peroxy compounds, hydroxylamine or mixtures thereof. Nitrate ions in the range of 0-20 g/l are advantageous. The pH value of the bath lies between 1.5 and 4, preferably between 2.5 and 3.5. Binary, ternary and even higher alloys can be deposited by the addition of Zn, Ni, Co, Fe or Mn salts. The metal ions may also be supplied to the electrolyte by anodic dissolution.

10 With respect to the conditions of the electrolysis, the electrolyte may be left at rest during the process or it may be moved. The current densities are at $> -1 \text{ A/dm}^2$ and preferably move in the range of approximately $j = -1$ to approximately $j = -100 \text{ A/dm}^2$. Current densities in the range of -5 to -50 A/dm^2 are particularly preferred. The temperature of the electrolyte amounts to $> 40^\circ\text{C}$, and is preferably in the range between 40 and 80°C , particularly preferred between 60
15 and 70°C .

As was mentioned before, the electrolysis process may be controlled in both a potentiostatic and a galvanostatic manner, either a direct current or a pulsed direct current being usable. The layer thickness distribution may be regulated by controlling the local current density, that is, by different shaping and/or current shielding. In this way, even geometrically exacting parts are
20 able to be coated.

Abstract Of The Disclosure

A method is shown for phosphating metal layers by electrolytic deposition from acid aqueous solutions which contain at least zinc ions and phosphate ions, while simultaneously applying direct current. Simultaneously with the depositing of the phosphating layer, an electrolytic
5 deposition of zinc takes place in the same electrolyte. The current density, in this context, is in the range of $> A/dm^2$.

Fig.